

The Higher Alcohols and Their Physical Constants

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY
JANE DICK MEYER

Baltimore
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ACKNOWLEDGMENT

The author wishes to express her deepest appreciation of the guidance and assistance of Dr. E. Emmet Reid at whose suggestion this work was undertaken. She also wishes to acknowledge the aid of Dr. D. H. Andrews not only in his willing discussions of her difficulties but also in his loaning of apparatus for the study of setting points. To Dr. Emil Ott she wishes to express her gratitude for helpful discussions on crystal forms. Her thanks are also due to Dr. A. B. F. Duncan who kindly loaned apparatus and laboratory room. She also wishes to thank Mr. F. O. Cockerille for his hearty coöperation in the work and for the use of his stills, and Dr. L. M. Ellis, Jr., and Mr. Thomas Gresham for their aid in setting up apparatus. She also wishes to acknowledge the coöperation of the stock room through Mrs. Neuhausen, which made it possible to carry on her work at night.



Isomorphism and Alternation in the Melting Points of the Normal Alcohols, Acetates, Bromides, Acids and Ethyl Esters from C₁₀ to C₁₈

The alternation of properties, particularly melting points, in various series has engaged the attention of many investigators.^{1,2,3} When the melting points of the normal alcohols are plotted against the number of carbon atoms a decided alternation is evident in the lower members but becomes so small for the higher that the scattered data in the literature are not sufficiently accurate and consistent to show whether it exists or not.

(1) (a) Timmermans, *Bull. soc. chim. Belg.*, **30**, 89-97; **31**, 389 (1922); **35**, 276-288 (1926); **38**, 295 (1929); (b) Defet, *ibid.*, **40**, 385-402 (1931); (c) Cuy, *J. Am. Chem. Soc.*, **42**, 503 (1920); (d) Pauly, *Z. anorg. allgem. Chem.*, **119**, 271-291 (1922); (e) Piper, Chibnall, Hopkins, Pollard, Smith and Williams, *Biochem. J.*, **25**, 2072-2094 (1931); (f) Garner and Randall, *J. Chem. Soc.*, **125**, 881 (1924); (g) Garner, Madden and Rushbrooke, *ibid.*, 2491 (1926); (h) Garner and Rushbrooke, *ibid.*, 1351-1359 (1927); (i) Garner and King, *ibid.*, 1849-1861 (1929); (j) King and Garner, *ibid.*, 578-580 (1931); (k) Malkin, *J. Am. Chem. Soc.*, **52**, 3739 (1930); (l) Malkin, *Nature*, **127**, 126-127 (1931); (m) Malkin, *J. Chem. Soc.*, 2796-2805 (1931); (n) Piper and Malkin, *Nature*, **126**, 278 (1930); (o) Whitby, *J. Chem. Soc.*, 1458 (1926); (p) Levene, West and Van der Scheer, *J. Biol. Chem.*, **20**, 521-534 (1915); **23**, 72; (q) Levene and Taylor, *ibid.*, **59**, 905-921 (1924); (r) Shepard, Henne and Midgley, *J. Am. Chem. Soc.*, **53**, 1948-1958 (1931); (s) Deese, *ibid.*, **53**, 3673-3682 (1931); (t) Verkade and Coops, *Rec. trav. chim.*, **46**, 903-917 (1927); (u) Blau, *Monatsh.*, **26**, 103 (1905); (v) Krafft, *Ber.*, **15**, 1714 (1882); (w) Gascard, *Compt. rend.*, **170**, 886-888, 1326-1328 (1920); *ibid.*, **153**, 1484-1487 (1911); *Ann. chim.*, [9] **15**, 347 (1921); (x) Bleyburg and Ulrich, *Ber.*, **64**, 2504-2513 (1913).

(2) Talvitie, *Ann. Acad. Sci. Fennicae*, No. 16, **A26**, 1-94 (1927).

(3) (a) Blaise and Guerin, *Bull. soc. chim.*, [3] **29**, 1903 (1903); (b) Jeffreys, *Am. Chem. J.*, **22**, 14 (1899); (c) Slotta and Jacobi, *J. prakt. Chem.*, [2] **120**, 249 (1929); (d) Fridau, *Ann.*, **83**, 1 (1852); (e) Oskerkko, *J. Russ. Phys.-Chem. Soc.*, **46**, 413 (1914); *Chem. Zentr.*, II, 1264 (1914); (f) Youtz, *J. Am. Chem. Soc.*, **47**, 2252 (1925); (g) Vorländer and Selke, *Z. physik. Chem.*, **129**, 435 (1927); (h) Piper and co-workers, *Biochem. J.*, **25**, 2072 (1931).

It seemed desirable to decide this question by preparing the normal alcohols from decyl to octadecyl in the highest purity practicable and determining their setting points by the most accurate method, using the same apparatus and temperature scale for all. For comparison the setting points of the acids and their ethyl esters, from which the alcohols were

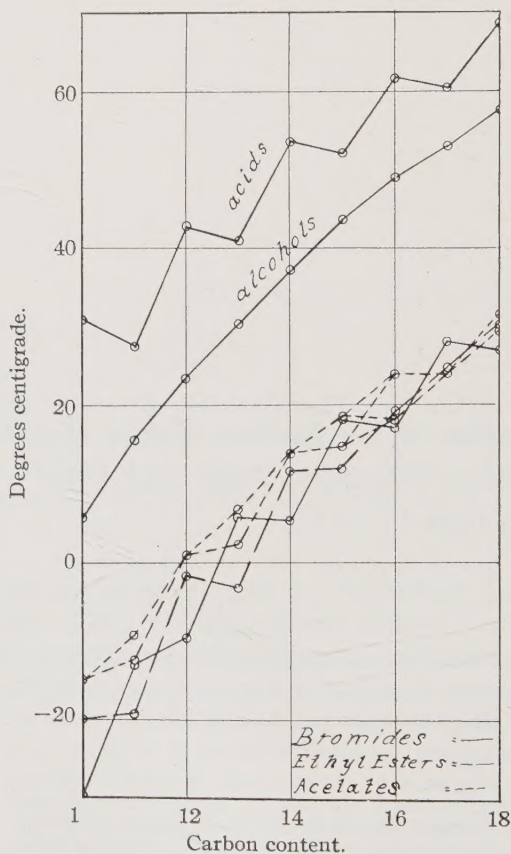


Fig. 1.—Melting points.

Deese¹⁸ found a transition in *n*-amyl bromide and Levene and Taylor¹⁹ speak of two forms of the nitriles.

When our work was almost finished, Phillips and Mumford⁷ published a paper on dimorphism of several of these compounds. They considered only cetyl and octadecyl alcohols and related compounds and also ethyl heptadecate. They found two types of dimorphism. Some of their

prepared, have been determined and also those of the bromides and acetates made from the alcohols. The melting points of many of these compounds, particularly those with uneven numbers of carbon atoms, were unknown.

In determining the setting point of cetyl alcohol a break in the cooling curve betrayed a transition in the solid state. This led to a study of the cooling curves for the other compounds and the discovery of polymorphism in a number of them. Garner and co-workers^{1f,g,h,i} have studied polymorphism in the acids by cooling curves, Francis, Piper and Malkin⁴ by x-rays and Malkin^{1k} by x-rays and optical methods. Huffman, Parks and Barmore⁵ and Garner, van Bibber and King⁶ find transitions in a number of hydrocarbons by thermal measurements.

(4) Francis, Piper and Malkin, *Proc. Roy. Soc. (London)*, **128A**, 214-252 (1930).

(5) Huffman, Parks and Barmore, *J. Am. Chem. Soc.*, **63**, 3876-3888 (1931).

(6) Garner, van Bibber and King, *J. Chem. Soc.*, 1533 (1931).

(7) Phillips and Mumford, *ibid.*, 1732 (1931).

compounds showed two distinct melting points corresponding to two crystal forms, while others showed a break in the cooling curve of the solid indicating a change in crystal structure. This was enantiotropic and could be observed in either a cooling curve or a melting curve of the solid. When two distinct melting points were obtained, the crystal which formed first and had the lower melting point was designated as an "alpha crystal," while that which formed second, having a higher melting point, was termed a "beta crystal." For an arrest in the cooling curve of the solid they used the term "gamma modification." For the sake of clearness this convention will be followed here. They found alpha and beta crystals for cetyl chloride, cetyl and octadecyl acetate, ethyl palmitate and stearate, and diethyl cetyl malonate. No dimorphism was found in cetyl bromide, or iodide, *n*-hexadecane or ethyl cetyl ether. Transitions of the gamma type appeared in cetyl alcohol and ethyl heptadecoate.

Since our work was finished (November, 1931), Malkin^{1m} has published a paper on the ethyl esters in which he finds enantiotropic dimorphism in ethyl heptadecoate and higher uneven ethyl esters and Phillips and Mumford⁸ have published a second paper considering the even esters C_{10} , C_{12} , C_{14} and C_{16} and C_{18} with one uneven ester, ethyl heptadecoate. They found no dimorphism for the lower even esters except ethyl myristate, for which they record an alpha fusion point of 11.7° and a beta melting point of 12.3° .

Smith⁹ also studied dimorphism in ethyl palmitate, ethyl stearate and butyl stearate, the first two of which give alpha and beta crystals while butyl stearate gives only one kind. In a very recent paper¹⁰ he discusses cetyl and octadecyl iodides and hexadecane and octadecane. From cool-

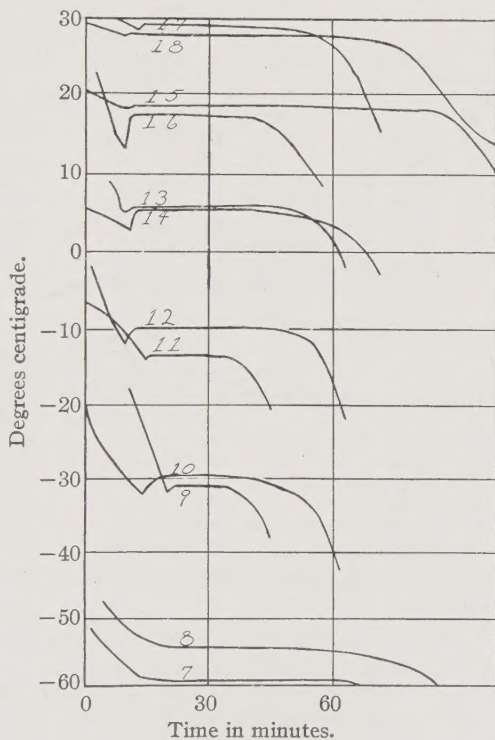


Fig. 2.—Bromides.

(8) Phillips and Mumford, *J. Chem. Soc.*, 898 (1932).

(9) Smith, *ibid.*, 804 (1931).

(10) Smith, *ibid.*, 737-741 (1932).

ing curves of the pure solids he does not find any evidence of polymorphism but from binary systems he finds indications of a transition in these compounds.

Results

Alternation.—The results obtained are brought together in Table I and in figures.

TABLE I
FUSION POINTS AND CRYSTAL FORMS, °C.

Carbon content	Alcohols— α Form stable			Bromides, fusion point		Acetates α Form (f. p.)			β Form (f. p.)	
	Transition			Ref.		Transition			Ref.	
10	5.99		9	-29.62		-15.05	S			
11	15.85		10	-13.15		-12.59	M	Monotropic	-9.27	
12	23.87		11	-9.60		1.13	S			
13	30.63	E 27.96-28.75	12	5.94		2.44	M	Monotropic	7.03	
14	37.62	E 34.58-35.33	13	5.67		14.01	S			20
15	43.84	E 37.33	14	18.63		14.99	M	Monotropic	18.77	
16	49.27	E 42.75-44.84	15	17.54	18	18.49	M	Monotropic	24.12	21
17	53.31	E 45.55-45.85	16	28.40		24.39	S			
18	57.85	E 51.93-52.89	17	27.35	19	29.97	M	Monotropic	31.95	22
	Acids— α Form stable			Hydrocarbons		α Form (f. p.)			β Form (f. p.)	
	Transition					Transition				
10	31.19		23	-29.76		-19.96	S			32
11	277.77	E 10.65-10.52	24	-25.65		-19.39	S			
12	43.22		25	-9.73		-1.68	S			33
13	41.55	E 28.09-27.59	26	-6.2		-3.13	S E	-11.94 to -12.26		
14	53.86		27	5.5		11.93	S			34
15	52.26	E 41.33-40.86	28	10		12.21	S E	8.44-8.24		
16	61.82		29	18.2		19.72	M	Monotropic	23.2 ^a	35
17	60.66	E 58.15	30	22.5		25.11	S E	17.04-16.23		36
18	68.82		31	27.90		30.56	M	Monotropic	32.9 ^a	37

^a Data taken from Phillips and Mumford. E = enantiotropic, S = stable, M = metastable.

The numbers refer to prior references, the *letters* to Ref. 1 (a = 1a; b = 1b, etc.).
⁹ 6.4° t and u; 7° 2. ¹⁰ 16.3° t; 11° z; 19° u and 3b. ¹¹ 23.8° t; 24-26° u; 24° v; 23° k. ¹² 30.5° u. ¹³ 37.7° h; 38° v, u and k. ¹⁴ 44° w; 45-46° u and 10. ¹⁵ 49.1° 5; 49° w and k; 49-49.5° u; 49.27° 8 and v. ¹⁶ 54° p and w. ¹⁷ 58.5° p and w; 59° v and k; 57.95° 8; 58.5-59.5° q. ¹⁸ 16.3° 5; 15-16° 3c; 15° 3d. ¹⁹ 28.5° 3e. ²⁰ 12-13° v. ²¹ 22-23° v; 22.7° 3f; α 18.7°, β 22.3° 5. ²² 31° v; α 29.7°, β 31.3° 5. ²³ 31.3° b; 31.4° g; 31° 3g and u. ²⁴ 26° 3b; 28.4°, g; 28.2°, i; 28° u. ²⁵ 43° u; 43.7°, g. ²⁶ 40.5° u, 41.6° g; 41.0° i; 44.5-45.5° p. ²⁷ 54° u, 2 and 3h; 53.7° g. ²⁸ 52.1° 2 and g; 52° h; 51° u; 52.5° 3h. ²⁹ 63.1° 2; 62.7° g; 62° u and 3g; 69.41° 7 and 8. ³⁰ 62.0° 2; 61.4° g; 60.7° i; 60 u. ³¹ 70.12; 70.65° g; 69° u and 3g; 69.41° 7 and 8. ³² -20.5° 5; -19.9° b. ³³ -2.0° 5; -10° u. ³⁴ 11.0° b; 10.5-11.5° u; α 11.7°, β 12.3° 5. ³⁵ α 19.2° 5; 19.4° 7 and 8; β 23.2° 5; 24.8° 7 and 8; 24° 3g; 25° 2; 24.2° u. ³⁶ 25.2° 5; 25° l and m; 28° 2; 27° u. ³⁷ α 30.4° 5; 30.92° 7 and 8; β 32.9° 5; 33.4° 7 and 8; 34° 2; 33.7° u; 33-34° q; 33° 3g.

From butyl to decyl the melting points of the even alcohols are on a slightly higher curve than those of the odd. This seems to continue with the higher alcohols but in spite of all our care the accuracy of our measurements is hardly great enough to make sure of this.

We have inserted in our table the melting points of the hydrocarbons as given in the literature. It is a remarkable fact that the even bromides and the hydrocarbons from which they are derived have almost the same melting points. It may be said that, as far as the melting point is concerned, a terminal bromine atom has the same effect as a methyl group since if the curve for the alkyl bromides were moved one space to the right it would almost coincide with the hydrocarbon curve. In the bromide series the alternation is the reverse of what it is in the others, the odd compounds having the high melting points. Beginning with C_{13} the odd melt higher than the next higher even.

The curve for the acetates is double since there are two forms for those of C_{11} , C_{13} , C_{15} , C_{16} and C_{18} . The melting points of the acetates and the isomeric ethyl esters are on very similar curves, both showing alternation. The differences between the melting points of the isomers show alternation but diminish as we go up the series; the acetates melt higher as far as C_{15} . For ethyl palmitate and stearate we obtained only the low melting forms but have plotted the data of Phillips and Mumford for the high.

Polymorphism.—From the time-temperature curves of the bromides, it is evident that there is no polymorphism. A transition was observed (Fig. 3) in the odd acids even during their preparation. When one of these acids in the molten condition is poured into water and cooled it first forms a solid cake, as the even acids do, but soon this would disintegrate with the formation of small, apparently denser, crystals which would remain suspended in the water. An uneven acid cooled in a glass container breaks away from the walls.

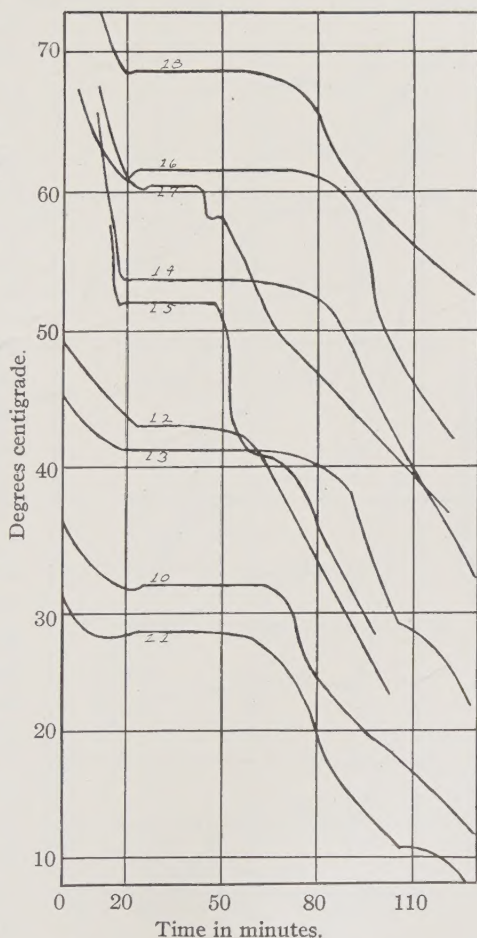


Fig. 3.—Acids.

The cooling curves for the acids are reproduced in Fig. 2. The transition temperature of margaric acid is near its setting point but this interval increases as we go down the series.

The polymorphism of the alcohols is shown in their cooling curves.

Decided arrests were found in the curves of all the alcohols down to dodecyl (Fig. 4). A change noticeable to the naked eye took place at

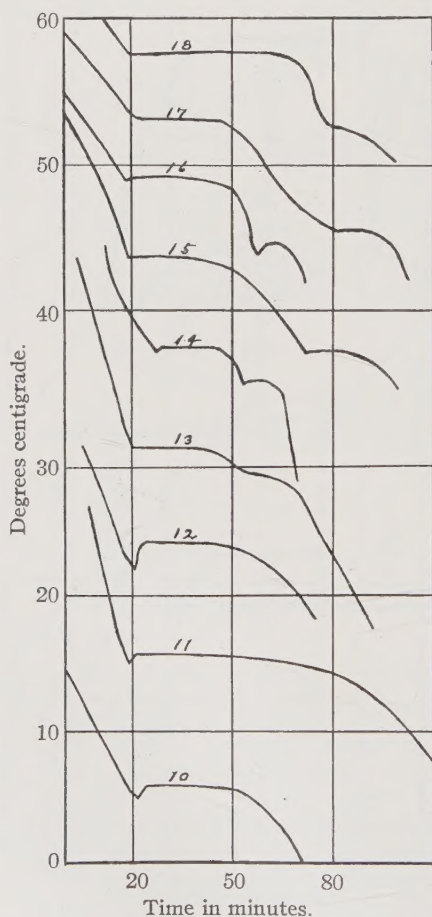


Fig. 4.—Alcohols.

this transition; the crystals first forming were transparent but at the transition point the melt became white and amorphous looking. For decyl, undecyl and dodecyl no arrest was found in the curve of the dry alcohol, but cooling the alcohol below zero seemed to introduce some impurity, for the alcohol would not then give a flat cooling curve but supercooled greatly and would show a peak below the original setting point and then come down. Alcohols showing this type of curve would also show a decided transition point. In the light of Garner, Madden and Rushbrooke's experience with acids containing a trace of water and the author's experience with wet uneven acids it seems logical to suppose that water is the impurity introduced by the low temperature. Thus the presence of the transition in the curve for these alcohols can be explained. The transition in the higher alcohols cannot be explained in this manner for they had been distilled. If the heat of this transition is less for lower members of the group, the

presence of the water might be necessary to make the change rapid enough to be noticeable. Malkin gives data only on even alcohols; in this work a transition was found not only for the even alcohols: tetradecyl, cetyl and octadecyl, but also for the uneven ones: tridecyl, pentadecyl and heptadecyl.

The acetates proved to be the most interesting compounds studied. For cetyl and octadecyl two fusion points were found, while heptadecyl

gave only one; but below cetyl it was the uneven acetates which gave two fusion points, while the even acetates displayed only one. Only one parallel occurrence was found: Francis, Piper and Malkin² find one crystal spacing shown by the uneven acids up to and including pentadecoic and by the even acids starting with palmitic. In plotting the fusion points of the acetates it seems as though the curve for the beta form of the acetates of uneven alcohols is continued in that of the beta form of the even acetates. And, likewise, the alpha form for the lower uneven acetates seems continued in that of the alpha form for the higher even acetates. The value for heptadecyl acetate lies on the curve for the alpha forms of the even acetates to whose cooling curves its cooling curve is similar. But the fusion points of the lower even acetates which have the same type of curve lie on a curve which is slightly above the curve for the beta form of the uneven acetates.

The cooling curves for these acetates are worthy of mention. The acetate cools until the alpha form begins to crystallize. It displays a flat curve until the substance is solid and then cools further, but soon the beta crystal begins to form and the curve will rise to the higher fusion point. If the melt is disturbed even slightly during the formation of the alpha crystals the cooling curve rises to the fusion point of the beta variety (Fig. 6).

With the alpha form for octadecyl and cetyl there was no supercooling; likewise with the acetates having only one fusion point—heptadecyl, tetradecyl, dodecyl and decyl. In order to obtain an accurate value for the beta form the melt was seeded with crystals cooled to the temperature of carbon dioxide snow on the end of a heavy sealed capillary, but even with such seeding and with vigorous stirring there was always consider-

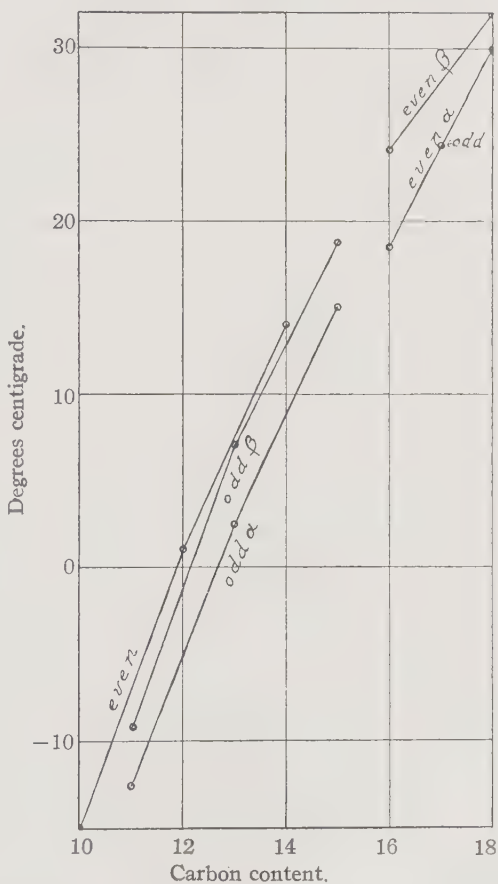


Fig. 5.—Melting points of acetates.

able supercooling with the beta varieties for either even or uneven acetates. Despite this supercooling it was possible to obtain reproducible values. In

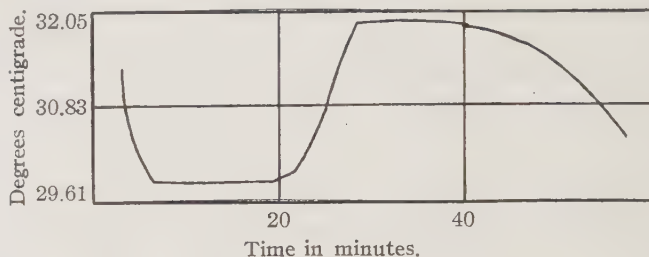


Fig. 6.—Cooling curve of octadecyl acetate.

the alpha variety of the uneven acetates there was also decided supercooling, but no attempt could be made to prevent this since to disturb the

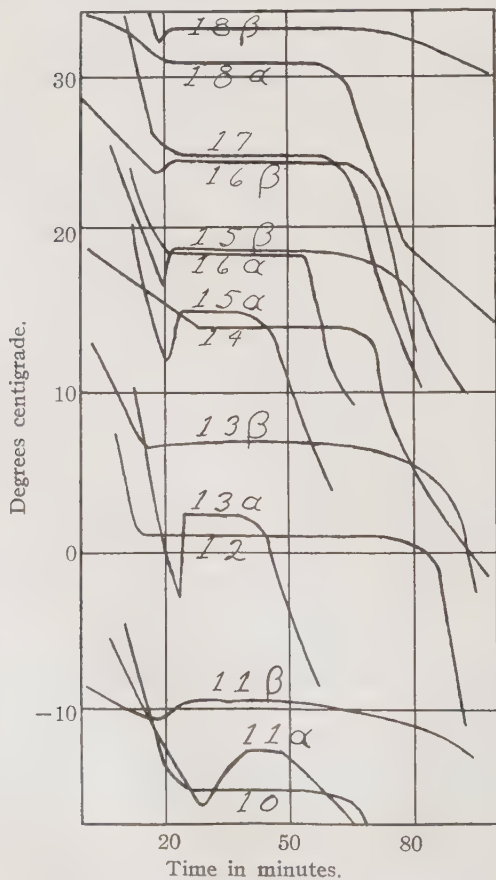


Fig. 7.—Acetates.

melt would cause the beta crystal to form. In spite of this, reproducible values for the fusion points could be obtained. In this mass of similarities and dissimilarities only an x-ray study can prove conclusively what forms are related, and whether we have to deal here with two forms, alpha and beta as here used, or whether there may be three, four or even more different crystal spacings.

The ethyl esters combine the two forms of dimorphism which have been found in these compounds by Smith¹⁰ and Phillips and Mumford.⁸ Malkin^{1m} in an x-ray study of ethyl and methyl esters found two forms for the ethyl esters, apparently alpha and gamma forms from his description. For the methyl esters he found that only those of the odd acids showed the two forms.

The crystals of ethyl palmitate and ethyl stearate which

are obtained by crystallizing from alcohol are of the higher melting variety. Smith, Phillips and Mumford used these crystals to seed the melt to obtain the fusion point of the beta variety. To obtain a true fusion point they kept the esters at the setting point for a long time until crystallization was finally accomplished. With the exception of these two articles there is no mention in the literature of the lower-melting crystalline form. If melting point measurements were made it would be easy to see why this is so because the crystals of an ester which had been well solidified or had been crystallized from ethyl alcohol would be of the beta variety.

In our work great difficulty was encountered in obtaining the setting points of these two ethyl esters. With ethyl stearate it was easy to obtain a cooling curve for the lower melting alpha crystal though the curve obtained began to fall too soon—and then fell too gradually. The lower part of the curve was of no value for the beta crystal began to form and made two successive humps in the curve. Phillips and Mumford also speak of getting a cooling curve for the alpha variety with retardation due to the formation of the beta crystal. The apparatus used by us did not permit keeping the ester at a certain temperature for any length of time so that it was impossible to obtain a fusion point for the beta crystal. With the palmitate it was difficult to get a curve for even the

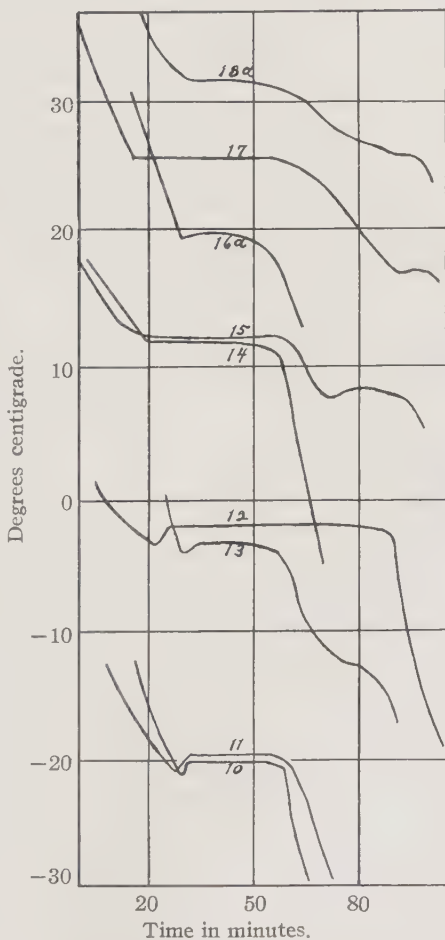


Fig. 8.—Ethyl esters.

alpha variety because the two crystals grew simultaneously. The lower melting crystal would start to form in long needles in the melt and then small clumps of much smaller compact would begin to grow and cause the temperature to rise. An inferior curve was thus obtained for the lower melting crystal but again it was impossible to obtain a curve for the higher melting variety. Since the higher melting point has been studied by many

workers it was thought more valuable for our purposes to obtain a value for the lower one. In the curves for the uneven esters transitions were found in the cooling curves of the solids of ethyl tridecoate, pentadecoate and heptadecoate.

Experimental

Preparation of Materials.—The compounds were prepared from 22.5 kilos of coconut oil which was saponified with 40% sodium hydroxide. To 4 kg. of the liberated acids, 4 liters of 95% alcohol and 825 g. of calcium chloride and hydrogen chloride gas were added and the mixture was heated for thirty-six hours. After cooling the aqueous layer was siphoned off and 140 g. of calcium chloride and more hydrogen chloride were added. After twelve more hours of heating the free acid was usually less than 2%. The ester layer was well washed with water and then with very dilute ammonia.

The mixture of esters was fractionated at 15 mm. at first through a simple column and then through a precision still of the Peters and Baker¹¹ type. The portion boiling higher than ethyl myristate was completely hydrogenated at 2 atm. pressure with a nickel catalyst. The fractionation was repeated until cuts were obtained which boiled constantly.

It was found best to convert the ethyl esters into butyl by heating them in excess butyl alcohol containing hydrogen chloride in the pot of a column still until the lower alcohol was eliminated.

The esters were reduced to the corresponding alcohols by a modification of the Beauveault and Blanc method.¹² The charge was 1.5 moles of the ester, 3 liters of butyl alcohol and 180 g. of sodium. When the reaction was over 160 cc. of water was added cautiously and the mixture heated for an hour to ensure saponification of any ester present. The mixture was cooled to 80° and 1200 cc. more water added. After agitation the butyl alcohol layer was separated and washed with two 500-cc. portions of 20% brine. To this was added a concentrated water solution of 40 g. of calcium chloride. The butyl alcohol was driven off by steam distillation and the hot mixture of alcohol and calcium soap poured into a large dish. The alcohol was extracted from the calcium soap with toluene, larger amounts being required for the higher alcohols. The yields of the alcohols were from 81 to 87%.

The bromides were prepared by passing gaseous hydrobromic acid into the alcohol kept at 140–150° or at 130° for the lower boiling alcohols. The water formed was carried over by the excess of the acid which was caught in a cold water trap along with some of the alcohol and bromide that were carried over; when no more water seemed to be evolved the alcohol-bromide mixture was cooled, poured into a pressure bottle and saturated with hydrogen bromide in the cold or at its melting point. The bottle was closed and heated for an hour at 150°. It is important to push the conversion as far as possible since if much of the alcohol is left emulsions are formed. The crude bromide was washed with sodium sulfate solution and then with concd. sulfuric acid as long as anything was removed, and again with the sodium sulfate solution. The yields were 84 to 96%. The bromides were further purified by fractionation. This method is an adaptation of that used by Moslinger,¹³ Guthzeit,¹⁴ Krafft¹⁵ and Adams and Dyer¹⁶ for iodides; and by Ruzicka, Stall and Schinz,¹⁷ and Oskerko¹⁸ for bromides.

(11) Peters and Baker, *Ind. Eng. Chem.*, **18**, 69 (1926).

(12) Beauveault and Blanc, *Compt. rend.*, **136**, 1676 (1903); **137**, 60 (1903).

(13) Moslinger, *Ann.*, **185**, 49 (1877).

(14) Guthzeit, *ibid.*, **206**, 351–367 (1881).

(15) Krafft, *Ber.*, **19**, 2984 (1886).

(16) Adams and Dyer, *J. Chem. Soc.*, **127**, 70–73 (1925).

(17) Ruzicka, Stall and Schinz, *Helv. Chim. Acta*, **11**, 670–686 (1928).

(18) Oskerko, *J. Russ. Phys.-Chem. Soc.*, **46**, 411–416 (1914).

The acetates were prepared by the usual method of heating the alcohol with acetic anhydride and fused sodium acetate.

The uneven acids were obtained through the nitriles which were prepared by the method of Adams and Marvel,¹⁹ heating seventy-two hours to complete the reaction. The purified nitrile was saponified by heating for twelve hours in butyl alcohol and sodium hydroxide. The butyl alcohol solution was washed with water to remove the excess alkali and treated with calcium chloride. The calcium soap was freed from butyl alcohol by steam distillation and from water by filtration, dried and then washed with toluene until it became fluffy and white. The acids were set free, well washed with hot water and converted into their ethyl esters which were then fractionated in the precision still. The yield from the bromides to the acids were 85-90%.

Apparatus

The time-temperature curves were made by the use of a copper-constantan thermocouple according to the method of Andrews, Kohman and Johnston.²⁰ The container for the melt was an adaptation of that described by Southard and Andrews.²¹ A type K potentiometer and sensitive galvanometer were used to measure the e. m. f. Temperatures below zero centigrade were determined from the scale of Southard and Andrews.²¹ For temperatures above 0°C. a scale contained in an unpublished part of the dissertation of R. H. Smith of this University was used. The thermocouples were carefully calibrated. The fusion points were checked and rechecked; an accuracy of one microvolt was obtained, which is in the neighborhood of 0.02°.

Summary

The normal primary alcohols from decyl to octadecyl, their acetates and the corresponding bromides and also the acids and their ethyl esters have been prepared and purified with care.

The setting points have been determined accurately. The melting points of the alcohols do not show detectable alternation but the bromides do. Many of the acetates and ethyl esters show dimorphism.

(19) Adams and Marvel, *J. Am. Chem. Soc.*, **42**, 299 (1920).

(20) Andrews, Kohman and Johnston, *J. Phys. Chem.*, **29**, 914 (1925).

(21) Southard and Andrews, *J. Franklin Inst.*, **207**, 3, 323-339 (1929).

BIOGRAPHY

The author, daughter of Paul A. and Jean M. Dick Meyer, was born in Greensburg, Pa. There she attended the grade schools and the city high school from which she graduated in June, 1924, with honors. She was matriculated at Wilson College in October, 1924, and graduated there in June, 1928, with an A.B. degree (with a major in chemistry and a minor in mathematics). In the fall of 1928 she entered The Johns Hopkins University. In February, 1930, she took up work on the subject of this dissertation under the guidance of Dr. E. Emmet Reid.

